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**TestAmerica, Inc.**

**Dayton Division**

**Standard Operating Procedure**

Analyte or Suite: Graphite Furnace Metals

Methodology: Perkin Elmer SIMAA 6000 Graphite Furnace

Reference: EPA SW-846, 3rd Edition, July 1992, 7000 series

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## GRAPHITE FURNACE METALS

# 1. INTRODUCTION AND SCOPE

1.1. Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters, and domestic and industrial wastes. Sample digestions should be performed according to the guidelines and procedures established within the individual digestion SOPs. While drinking waters and filtered groundwaters are free of particulate matter, turbidity, and odor may be analyzed directly, domestic and industrial wastes require processing to solubilize suspended material. Sludges, sediments and other solid type samples may also be analyzed after proper pretreatment. If the analyte concentration is greater than the linear range of the instrument, ICP atomic absorption may be a more appropriate analytical procedure.

1.2. Detection limits, sensitivity and optimum ranges of the metals will vary with the various makes and models of satisfactory atomic absorption spectrophotometers. The measurable concentration ranges are somewhat dependent on equipment such as the type of spectrophotometer, the energy source and the degree of electrical expansion of the output signal. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To insure valid data with furnace techniques, the analyst must examine each matrix for interference effects and if detected treat accordingly using either successive dilution, matrix modification or method of standard additions.

# 2. SUMMARY OF METHOD

## 2.1. Definition of Terms

2.1.1. **Optimum Concentration Range:** A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operation condition employed.

2.1.2. **Sensitivity:** The concentration in milligrams of metal per liter that produces an absorption of 1% (or equivalently an absorbance of about 0.0044). Also referred to as characteristic concentration.

2.1.3. **Detection Limit:** Detection limits can be expressed as either an instrument or method parameter. The limiting factor of the former using acid water standards would be the signal to noise ratio and degree of scale expansion used; while the latter would be more affected by the sample matrix and preparation procedure used.

2.1.4. **Reporting Limit (RL):** The concentration of metals, above which, a value is reported to the client; otherwise "<" the reporting limit is reported. The reporting limit will generally be a specified multiple of the detection limit.

2.1.5. **Dissolved Metals:** Those constituents (metals) which will pass through a 0.45 u membrane filter.

2.1.6. **Suspended Metals:** Those constituents (metals) which are retained by a 0.45 u membrane filter.

2.1.7. **Total Metals:** The concentration of metals in an unfiltered sample following vigorous digestion or the sum of the concentrations of metals in both the dissolved and suspended fractions.

## 2.2. Introduction to Atomic Absorption Spectroscopy

In direct aspiration atomic absorption spectroscopy (FLAAS) a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp whose cathode is made of the element to be determined is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy. The difference between GFAA and FLAA is the manner in which the sample is introduced and atomized.

## 2.3. The Furnace

A graphite tube is normally the heating element of the graphite furnace. The cylindrical tube is aligned horizontally in the optical path of the spectrometer and serves as the spectrometer sampling cell. A few microliters (usually 5-50) of sample is measured and dispensed through a hole in the center of the tube wall onto the inner tube graphite platform. The tube is held in place between two graphite contact cylinders, which provide electrical connection. An electrical potential applied to the contacts causes current to flow through the tube, the effect of which is heating of the tube and the sample.[1]

The sample is evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms are vaporized and dissociated for absorption in the tube than the flame, the use of small sample volumes or detection of low concentrations of

elements is possible.

> The entire assembly is mounted within an enclosed, water-cooled housing. Quartz windows at each end of the housing allow light to pass through the tube. The heated graphite is protected from air oxidation by the end windows and two streams of argon. An external gas flow surrounds the outside of the tube, and a separately controllable internal gas flow purges the inside of the tube. The system should regulate the internal gas flow so that the internal flow interrupted during atomization. This helps to maximize sample residence time in the tube and increase the measurement signal.[2]

Note: Alternative gas is nitrogen with hydrogen (5%). This is used in the beginning furnace steps. It must be off before atomization step.

## 3. SAFETY

3.1. Each employee is directly responsible for complete awareness of all health hazards associated with every chemical that he/she uses. The employee must be aware of these hazards, and all associated protective wear and spill clean-up procedures PRIOR TO THE USE of any chemical. In all cases, both the applicable MSDS and supervisor or Safety Officer should be consulted. The employee should comply with all safety policies as presented in the NET Safety Manual. The bottle labels also provide important information that must be noted. If you have any questions, consult your supervisor or safety officer.

Personnel performing this procedure may be working with flammables, poisons, toxics, carcinogens, teratogens, mutagens, and biohazards. In particular, approved gloves, safety glasses, and labcoats must be worn, and solvents will be handled in ventilated hoods, in addition to other measures prescribed by the Division. It should be noted that samples must be handled with as much care as any of the materials used in this method due to the unknown nature of their composition.

3.2. Gases commonly used with GFAA include argon or nitrogen, and argon/hydrogen (5%). High pressure gas cylinders can be dangerous if mishandled.

3.2.1. Move gas cylinders with an approved handcart after insuring that the valve cap is secured.

3.2.2. Store gas cylinders in a vertical position only. Fasten securely to an immovable bulkhead or a permanent wall.

3.2.3. When gas cylinders are stored in confined areas, such as a small storage room, ventilation should be adequate to prevent toxic or explosive accumulations of gas.

3.2.4. Locate gas cylinders away from heat or ignition sources. Cylinders have a pressure-relief device which will release the contents of the cylinder if the temperature exceeds 52°C.

3.2.5. When the equipment is turned off at the end of the work day, close all gas cylinder valves tightly at the tank. Bleed the remainder of the line to the atmosphere before the exhaust fan is turned off. This is the preferred procedure. In some cases, it may not be possible to do this due to overnight runs and/or configuration of gas lines.

3.2.6. Perform periodic gas leak tests by applying a soap solution to all joints and seals. Recommended minimum frequency is once per week and/or whenever a tank is changed.-

3.3. See manufacturer's instruction for proper installation of drain vessel.

3.4. Smoke and vapors from the furnace should be vented according to manufacturer's recommendations.

3.5. Do not look directly at the light from the hollow cathode or EDL lamps. Though they may not appear "bright", invisible ultraviolet radiation can damage the eyes. Also, looking at an incadescent graphite tube is discouraged.

3.6. Be cautious when handling the graphite tube after atomization. You might burn yourself.

## 4. REAGENTS AND MATERIALS

### 4.1. Apparatus

The following apparatus is recommended for performing this procedure. Equivalent items should only be used as a last resort or when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. When an equivalent is used in place of the recommended apparatus, this deviation does not have to be defined in the division specific appendix. However, it is important to report any item which results in an improvement to the corporate technical support team so that they can assist in the distribution of Best Developed Practice (BDP).

4.1.1. The SIMAA 6000 spectrometer from Perkin-Elmer is a high performance atomic absorption spectrometer, specially designed for simultaneous multi-element, graphite furnace analyses. It is capable of fully automatic, single or multi-element analyses. The spectrometer and atomizer control, and the display and manipulation of data are all performed through the computer.

4.1.2. Pyrolitically coated graphite tubes or platforms.

4.1.3. Hollow cathode lamps: Single element lamps are to be preferred but multi-element lamps may be used. Electrodeless discharge lamps may also be used when necessary. Some elements, namely Sb, Tl, Pb, Sn, are not easily analyzed by the hollow cathode lamps. In those cases, the electrode-less discharge lamp (EDL) might prove a better analyzer.

4.1.4. Electrodeless discharge lamps: These lamps may provide better sensitivity, greater intensity, higher absorbances, and lower gain.

4.1.5. Pipets: Macro (Oxford) and micro (Eppendorf) pipets with disposable tips.

Oxford pipet 1-5 mL / pipet tip Oxford pipet 5-10 mL / pipet tip Eppendorf pipets 1-250 uL and tips

4.1.6. Glassware: All glassware should be washed with detergent, rinsed with tap water, dilute nitric acid, and rinsed three times with deionized distilled water. The concentration of the nitric acid should be at least 10%. Standard Methods, 18th Edition recommends the use of 1 + 1 nitric, 1 + 1 hydrochloric, or aqua regia.

**4.2. Reagents**

The following reagents are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same.

All reagents must be properly labeled with the reagent identification and concentration, date prepared, expiration date, initials of analyst, and applicable safety information. Labels are available through the centralized purchasing system. The label has a place for the NFPA diamond, which will be used to indicate health (blue), flammability (red), reactivity (yellow), and contact/special (white) information obtained from applicable Material Safety Data Sheets (MSDS) supplied by the vendor.

4.2.1. Deionized water: Prepare by passing water through a mixed bed of cation and anion exchange resins or an equivalent source. Use deionized water for the preparation of all reagents, calibration standards, and dilution water.

4.2.2. Nitric acid (concentrated): If metal impurities are found to be present, use a spectrograde acid.

$HNO_3$ NFPA diamond: health = 3, flammability = 0, reactivity = 3, contact = 4.

Strong oxidizer! Contact with other material may cause fire.

Liquid and vapor cause severe burns. May be fatal if swallowed. Harmful if inhaled and may cause delayed lung injury. Keep from contact with clothing and other combustible materials. Do not get in eyes, on skin.

4.2.3. Nitric Acid (1:1): prepare a 1:1 dilution with deionized water by adding the concentrated acid to an equal volume of water.

NOTE: Acids used in the preparation of standards and for sample processing must be reagent grade or better.

4.2.4. Gases: Argon (or nitrogen) and the Argon and 5% mix should be of high purity.

4.2.5. Modifier: All methods use a 0.1% pd with 0.06% mg(NO3)2.

4.2.6. Snoop Leak Detector: Supelco Catalogue no. 2-0434.

**4.3. Standards**

The following standards are recommended for performing this procedure. The use of alternative standards will be allowed as long as they are of equal or greater quality and there is an associated improvement in efficiency, productivity, or cost.

4.3.1. Stock standard metal solutions: Commercially available stock standard solutions are to be used. The stock solutions are purchased at concentrations of 1000 mg/L or greater.

CAUTION: Many metals are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling stock solutions.

4.3.2. Working standard: A working standard solution is prepared by the dilution of the appropriate stock metal solution to cover the concentration range desired.

4.3.3 Calibration standard: A calibration standard solution is volumetrically prepared from the working standard solution. Refer to Appendix 1 for final concentration of all metals present in the solution.

4.3.3.1. A generic formula is based upon the proportion, C1V1 = C2V2

where:

C1 = Concentration 1 C2 = Concentration 2
V1 = Volume 1 V2 = Volume 2

Example: $\frac{1000 \text{ mg/L stock standard} \times 1 \text{ mL}}{100 \text{ mL final volume}}$ = 10 mg/L standard

4.3.4. Independent Calibration Verification Standards (ICVS). For each metal analyzed, it is necessary to obtain and analyze an

ICVS following each metal calibration. The ICVS is a standard obtained from a second source which is used for curve verification.

### 4.4. Blanks

4.4.1. Two types of blanks are required for the analysis. The calibration blank or reagent blank is used in establishing the analytical curve. The reagent blank should contain the same amount of acid as the standards used for instrument calibration. The procedure blank is used to monitor for possible contamination resulting from varying amounts of the acids used in the sample preparation.

4.4.2. Dilution water should contain the same acid concentration as the standards and blank used for instrument calibration.

4.4.3. If the sample analysis solution has a different acid concentration from that of the calibrating standards or blank, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

## 5. INTERFERENCES

### 5.1. Chemical and Matrix Interferences

5.1.1. Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in a inert atmosphere, the technique is still subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. If necessary, one way to help verify the absence of matrix or chemical interference use the following procedure.

5.1.1.2. Withdraw from the sample two equal aliquots. To one of the aliquots add a known amount of analyte and dilute both aliquots to the same predetermined volume. [The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1:4 while keeping in mind the concentration range of the analysis. Under no circumstances should the dilution be less than 1:1]. The diluted aliquots should then be analyzed and the unspiked results multiplied by the dilution factor should be compared to the original determination.

5.1.1.3. Agreement of the results (within $\pm$ 10%) indicates the absence of interference. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis. Those samples which indicate the presence of interference, should be successively diluted and reanalyzed to

determine if the interference can be eliminated. Also the matrix of the sample should be modified in the furnace.

5.1.2. Background Absorption: This is the result of nonspecific molecular absorption or light scattering caused by undissociated sample matrix components in the light path at atomization. Background absorption can be reduced through matrix modification, furnace programs, and Zeeman background correction.

5.1.2.1. Zeeman Background Correction: Zeeman can correct for higher and spectrally complicated background absorption. Zeeman corrects for the background absorption exactly where the original line source is located.

The Zeeman Correction is based on the principle that when an atom is placed in a strong magnetic field, its electronic energy levels are changed, thereby changing the atomic spectra which are a measure of these energy levels. Thus, instead of getting a single line in the absorption spectrum, when observed with polarized light, there are two inverse peaks (pointing down) at an equal offset on either side of the original peak. The spectral nature of background absorption is unaffected by the magnetic field. By placing the poles of an electromagnet around the atomizer and making alternating measurements, the uncorrected total and background absorbances can be made. The Zeeman correction takes the two side peaks out of the calculation of area by subtracting a spectrum with the magnet off from a spectrum with the magnet on.

5.1.3. Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however to prevent loss of the analysis element.

5.1.4. Samples containing large amounts of organic materials should be oxidized by conventional acid digestion prior to being placed in the furnace. In this way broad band absorption will be minimized.

5.1.5. From anion interference studies in the graphite furnace it is generally accepted that nitrate is the preferred anion. Therefore nitric acid is preferable for the digestion and solubilization step. If another acid in addition to HNO3 is required, a minimum amount should be used. This applies particularly to hydrochloric, and to a lesser extent, to sulfuric and phosphoric acids.

5.1.6. Carbide formation resulting from the chemical environment of the furnace has been observed with certain elements that form carbides at high temperatures. When this takes place, the metal will be released very slowly from the carbide as atomization continues. This problem is greatly reduced and the sensitivity increased with the use of pyrolytically-coated graphite.

### 5.2. Ionization Interferences

Ionization interferences have to date not been reported with furnace techniques.

### 5.3. Spectral Interferences

Although quite rare, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Also, interference can occur when resonant energy from another element in a multi-element lamp of a metal impurity in the lamp cathode falls within the bandpass of the slit setting and that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

### 5.4. Contamination

Contamination of the sample can be a major source of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be thoroughly cleaned. Pipet tips have been known to be a source of contamination. If suspected, they should be acid soaked with 1:5 $HNO_3$ and rinsed thoroughly with tap and deionized water. The use of a better grade pipet tip can greatly reduce this problem. It is very important that special attention be given to reagent blanks in both analysis and the correction of analytical results. Lastly, pyrolytic graphite because of the production process and handling can become contaminated. As many as five to possibly ten high temperature burns may be required to clean the tube before use.

## 6. ANALYTICAL PROCEDURES

### 6.1. Preservation and Handling

6.1.1. For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption, thus the collection and treatment of the sample prior to analysis requires particular attention. The quality control program should document through the use of spiked samples, reagent and sample blanks, that cleaning procedures are adequate. Care should be taken to verify the fact that the containers in which acid digested samples, blanks, and standards are packaged do not contribute contaminants. Before collection of the sample

a decision must be made as to the type of data desired, i.e., dissolved, suspended, or total.

6.1.2. All metals samples (except Cr VI and organic lead) must be acidified to a pH < 2 using 1 part nitric acid to 2.5 parts water - approximately 2.5 mL. This technique ensures compliance with DOT regulations. Metals analyses should be conducted within six months.

6.1.2.1. When pre-preserved sample containers have been used for sample collection, it is the responsibility of the analyst to verify adequacy of preservation at the time the actual analysis is initiated.

6.1.3. For the determination of dissolved constituents the sample must be filtered through a 0.45 u membrane filter as soon as practical after collection. A glass fiber pre-filter may be used in combination with the 0.45 u membrane filter. Glass or plastic filtering apparatus using membrane filters are recommended to avoid possible contamination. The filtering apparatus should be acid washed prior to use and in between samples. Use the first 50-100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 $HNO_3$ to a pH of <2. Normally, 2-3 mL of (1:1) acid per liter should be sufficient to preserve the sample. Analyses performed on a sample so treated shall be reported as "dissolved" concentrations.

## 6.2. Instrument Calibration

6.2.1. Preparation of a curve - daily (not referenced): The data used in plotting a daily calibration curve will consist of a blank and three standards evenly distributed throughout the range of the method. Prepare a standard curve by plotting the absorbance values of standards (y-axis) versus the corresponding concentrations (x-axis).

6.2.2. Calibration criteria as detailed in Section 7.4. must be met.

6.2.2.1. Verify the curve by analyzing an Initial Calibration Verification Standard (ICVS) as detailed in Section 7.5.

## 6.3. Daily Analytical Sequence

6.3.1. Calibration Curve: see Section 7.4.

6.3.2. Initial Calibration Verification Standards (ICVS): see Section 7.5.

6.3.3. Reporting Limit Verification Standard (RLVS): see Section 7.11.

6.3.4. Reagent Blank (RB): see Section 7.6.

6.3.5. Continuing Calibration Verification Standard (CCVS): see Section 7.7.

6.3.6. Preparation Blank (PB): see Section 7.8.

6.3.7. Lab Control Standard (LCS): see Section 7.9.

6.3.8. Matrix Spike/Matrix Spike Duplicate: see Section 7.10.

6.3.9. Samples 1-10

6.3.10. RB

6.3.11. CCVS

6.3.12. Samples 11-20

6.3.13. RB

6.3.14. CCVS

6.3.15. Complete steps 11 - 13 for all remaining samples (in groups of ten only)

6.3.16. Always end the sequence with a CCB and a CCV.

6.3.17. A continuing calibration verification (CCV) and continuing calibration blank (CCB) should be run after every tenth sample injection. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Tube life depends on sample matrix and atomization temperature. A conservative estimate would be that tube will last at least 400 firings.

## 6.4. Development of Analytical Programs

The objective is to select operating parameters which will completely desolvate the sample, remove the maximum amount of matrix material during the ash stage, provide adequate analytical sensitivity, and separate the analyte peak from the non-atomic absorption peaks.[3]

6.4.1. Drying: The purpose of this step is to remove the solvent from the sample. The sample must be dried at a sufficiently low temperature to avoid sample spattering. The sample must not boil. Sample spreading and/or spattering will result in reduced precision and is caused by temperatures which are too high. The temperature and time associated with drying depends on the nature of the solvent and the sample volume. The temperature is set near, but below, the boiling point of the solvent. The use of a ramping program provides a variable time over which the temperature is increased. Approximately 1-3 seconds per microliter of sample is required for complete drying.

Temperatures around 110°-130° C are routine for aqueous solutions. The use of platforms will result in the use of higher drying temperatures, due to the fact that, the platform does not reach as high a temperature as the wall of the graphite tube.

6.4.2. Pyrolysis or Ashing: The purpose of this step is to selectively volatilize inorganic and organic matrix components, which tend to give background absorption, from the sample. The analyte is in a less complex matrix after ashing. The temperature is increased as high as necessary to volatilize matrix components without loss of analyte. The temperature selected for the ashing step will depend on the analyte and the matrix. Do not use a temperature which greatly exceeds that required to accomplish the task. The life of the graphite tube is reduced with very high temperatures. The use of a ramping program is an option. Approximately 10-30 seconds is required for ashing. Temperature range for ashing is 300-1400°C.

6.4.3. Cool Down: Sometimes, a cool down step is necessary prior to atomization. The heating rate is a function of the temperature range to be covered. As the temperature range is increased, the rate of heating also increases. The use of a cool down step maximizes the heating rate.

6.4.4. Atomization: The purpose of this step is to produce free atoms to be measured and quantified. Atomization temperatures are analyte specific, and may vary slightly from matrix to matrix. The atomization temperatures and rate of heating affect the sensitivity of the analysis. If platforms are being used, rapid heating is desirable resulting in a zero ramp time. If ramping is being used for the temperature, consult the manufacturer's recommendations. The optimum temperature will be the lowest temperature giving the maximum absorbance. The lifetime of the graphite tube is prolonged at lower temperatures. The internal gas flow is usually interrupted during this step.

6.4.5. Cleanout Cool Down: After atomization, the graphite furnace may be heated to higher temperatures to burn off any sample residue which may remain in the furnace. The cool down step is usually needed when using platforms. The gas should be on during this step.

6.4.6. Gas Flow: The preferred gas is argon at 99.99% purity. The flow of gas through and around the graphite tube remove sample components from the atomizer at each step of the analysis. The gas flow may be reduced or increased at various points within the analysis to achieve a certain effect. Maximum gas flow during the drying and ashing steps will provide the most efficient removal of the products. Zero gas flow during the atomization step will increase the residence time of the analyte in the furnace.

6.4.7. Injection Volume: The typical injection volume is 20 uL. Smaller injection volumes decrease sensitivity and larger injection volumes increase sensitivity in approximate proportions

to the volumes used. The maximum injection volume is 50 uL (sample + modifier). Keep the volumes the same for instrument calibration and sample analysis in order to maintain a consistent spread within the graphite tube. The volume of modifier used should remain consistent. If the volume of modifier used is changed, it would not cause a dilution or concentration effect, since the dried mass of analyte remains the same. The volume of blank added to the standard or sample is adjusted appropriately keeping the total volume consistent. If possible, the sample volume should be kept the same as the highest standard volume. If the sample volume is reduced, then a dilution has been made and must be taken into account during calculation of results.

6.4.8. Peak Area vs. Peak Height

6.4.8.1. Peak height measures the maximum atom population which occurs during atomization and does not take matrix affects into account. Peak height is more sensitive and less accurate than peak area. Peak area permits integration of absorbance during atomization. The precision obtained from peak area is better. If the required sensitivity can be obtained from peak area, then peak area should be used rather than peak height. This choice can be roughly evaluated as follows:

$$\%RSD \times mean = SD$$

where: %RSD = Percent Standard Deviation

If the SD calculates high, it wouldn't be wise to use peak height, even if sensitivity is improved.

6.4.8.2. Peak area measurements are affected by baseline drift. SIMAA 6000 utilizes baseline offset correction (BOC) as a means for correcting for baseline drift. BOC measures the instrument baseline reading immediately prior to atomization and corrects the peak area integration accordingly.

6.4.9. Graphite Tubes: Pyrolitically coated graphite tubes have a dense, impervious surface, which resists hot gases and oxidation. Generally, these tubes are unreactive and have a reduced tendency to form carbides.

6.4.10. Modifiers: Modifiers increase matrix volatility or decrease analyte volatility, resulting in additional flexibility in the development of a furnace program, which yields the desired result. The use of matrix modifiers will require changes in the temperature program.

## 6.5. Calculations

6.5.1. The raw data is calculated based upon several criteria: the type of matrix involved; if a dilution or concentration of the sample was required; and the weights or volumes used for the initial preparation of the sample.

6.5.2. For GFAA, the raw data is in ug/L and may need to be converted to mg/L. The ug/L unit can be converted to mg/L by dividing by 1,000 (i.e. Moving the decimal point three places to the left). To determine the final value, however, consideration must be given to how the sample was prepared. The preparation of the sample is dependent upon the sample matrix.

6.5.2.1. If a sample is aqueous and no dilution or concentration is required (a standard preparation of 50 mL to 50 mL or 50:50 was employed), then the reported value is that which the instrument generated.

6.5.3. Dilutions

6.5.3.1. In the case where a dilution is performed (for example, a sample dilution of 50 mL to 100 mL), the dilution factor must be considered. For example:

The instrument shows an instrument reading of 0.200 mg/L

The final concentration would be determined by the following equation.

$$\frac{0.200 \text{ mg/L} \times 100 \text{ mL (Final Volume)}}{50 \text{ mL (Initial Volume)}} = 0.400 \text{ mg/L}$$

6.5.3.2. A dilution may be made at the time of analysis. A dilution is performed on a sample if the concentration is found to be out of calibration range. The dilution factor is written next to the sample identification with a notation such as 1:10, for a 1 mL to 10 mL dilution made. In calculating, this dilution factor must also be included in the calculation:

$$0.400 \text{ mg/L} \times 10 = 4.00 \text{ mg/L}$$

6.5.4. Concentration

If a concentration is required (200:10) then the concentration factor must be accounted for in the calculations.

$$\frac{0.200 \text{ mg/L} \times 10 \text{ mL (Final Volume)}}{200 \text{ mL (Initial Volume)}} = 0.010 \text{ mg/L}$$

6.5.5. Punctuation, Capitalization, Significant Figures

Attention to punctuation, capitalization and significant figures are necessary when reporting results. Examples of these are presented below.

6.5.5.1. A zero preceding the decimal is required in all instances.

6.5.5.2. Commas are used when reporting numbers in the thousands or greater.

6.5.5.3. Report units such as mg/Kg or mg/L with the K in Kg and L being capitalized.

6.5.6. Correlation Coefficient

The SIMAA 6000 software calculates the correlation coefficient and prints it out for each element analyzed. An acceptable correlation coefficient should be > or = 0.995.

6.5.7. Accuracy

Accuracy is determined by the percent recovery from a true or known value.

$$\text{Percent Recovery} = \frac{\text{Calculated Value}}{\text{True Value}} \times 100$$

6.5.8. Analytical Spikes

Analytical Spikes performed at the instrument are calculated as follows. A sample for Ag has a reading of 0.010 mg/L with no spike added. The sample is to be spiked with 0.5 mL per 10 mL sample with 0.20 mg/L Ag. This spike sample was analyzed and the reading was 0.020 mg/L. The calculation of the percent recovery is as follows:

$$\frac{0.020 \text{ mg/L} - 0.010 \text{ mg/L}}{0.0095 \text{ mg/L (actual spike added)}} \times 100 = 105\ \%$$

6.5.9. Matrix Spike

6.5.9.1. Another type of analyte spike is the matrix spike. For this type of spike there is no dilution of the original sample. A sample was analyzed for Pb. The concentration for the sample was 0.560 mg/L. A 1.00 mg/L spike was added to another aliquot of the sample with the same volume as the original digestate and digested. The sample is poured up to the same final volume. The concentration of Pb for the Matrix spike was 1.24 mg/L. The percent recovery is calculated as follows:

$$\%\ \text{Recovery} = \frac{1.24 \text{ mg/L} - 0.560}{1.00 \text{ mg/L}} \times 100 = 67\ \%$$

6.5.9.2. For digested spikes with a weight of original sample the calculation is done as follows:

The instrument reading of Al in a soil sample with a weight of 1.4561 g was determined to be 2.50 mg/L. The sample was poured up to 100 mL final volume. Another aliquot of the soil with a weight of 1.8761 g was spiked with 2.00 mg/L of Al and also poured up to 100 mL final volume. The instrument reading for the spiked sample was 5.11 mg/L. The calculation of the percent recovery of the spike is as follows:

First we need to calculate the instrument reading obtained per gram of the sample.

$$A = \frac{2.50 \text{ mg/L (Sample Reading)}}{1.4561 \text{ g (Sample Weight)}} = 1.7169 \text{ mg/L per gram sample}$$

Next we calculate the reading that should have been obtained for the sample weight used for the spiked sample.

1.8761 g (spiked sample aliquot) X A = 3.22 mg/L

The percent recovery is then:

$$\frac{5.11 \text{ mg/L (spike sample reading)} - 3.22}{2.00 \text{ mg/l (Spike concentration)}} \times 100 = 95\%$$

6.5.10. Precision

Precision of an analytical system is determined by calculating the relative percent difference (RPD) between two analyses of the same sample.

$$RPD = \frac{(\text{Reading \# 1}) - (\text{Reading \# 2})}{\frac{\text{Reading \# 1} + \text{Reading \# 2}}{2}} \times 100$$

otherwise known as: $\frac{\text{Difference}}{\text{Average}} \times 100$

6.5.11. Other Calculations

6.5.11.1. Filters:

(conc. mg/L) X (volume L/filter) = mg/filter
(0.02 mg/L) X (0.050 L/filter) = 0.001 mg/filter
Note: normally reported in ug/filter

6.5.11.2. Dry Weight: $\frac{(\text{conc. mg/L}) \times (\text{L})}{\frac{\text{wet weight}}{\% \text{ solids}}}$

6.5.12. Rounding Off

Round off by dropping digits that are not significant. If the digit 6, 7, 8, or 9 is dropped, increase preceding digit by one unit; if the digit 5 is dropped, round off preceding digit to the nearest even number: thus 2.25 becomes 2.2 and 2.35 becomes 2.4.

As a practical operating rule, round off the result of a calculation in which several numbers are multiplied or divided to as few significant figures as are present in the factor with the

fewest significant figures. (SW-846, Method 1050B)

6.5.13. Maintenance

Daily or as needed:

-check for a sufficient gas supply
-empty waste container
-check graphite tube and electrodes for wear and replace if worn
-clean windows and sample compartment with alcohol moistened optical tissue
-check capillary tubing for fit, cleanliness and tip squarely cut
-inspect graphite tube for wear and graphite shrouds for deposits
-replace fume extraction unit water and filter

# 7. QUALITY CONTROL

The following details the QC requirements which apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either instrument performance, method performance (including sample preparation), or individual sample performance. Our goal is to produce data of unquestionable quality. Always remember what purpose the QCI serves when evaluating QCI results. Guidelines can be provided, and are provided, but they cannot take the place of a logistical, common-sense evaluation of the complete data set.

For information on preparation of QCI solutions, refer to Appendix 1.

## 7.1. Method Detection Limits and Reporting Limits

An MDL study, following the MDL SOP, must be done during initial method validation and then annually. If the analytical method is changed, an MDL study must be done again. Also, the calculated MDL must not exceed the reporting limit. The current nominal reporting limits for this method are listed in Table 1.

**Table 1.**

| Element | Wavelength (nm) | Reporting Limit (mg/L) |
|---|---|---|
| Arsenic | 193.7 | 0.005 |
| Antimony | 217.6 | 0.020 |
| Beryllium | 234.9 | 0.001 |
| Cadmium | 228.8 | 0.001 |
| Chromium | 357.9 | 0.002 |

**Table 1.** Continued

| Element | Wavelength (nm) | Reporting Limit (mg/L) |
|---|---|---|
| Cobalt | 242.5 | 0.005 |
| Lead | 283.3 | 0.005 |
| Selenium | 196.0 | 0.005 |
| Silver | 328.1 | 0.001 |
| Thallium | 276.8 | 0.010 |

## 7.2. Method Validation Sample (MVS)

### 7.2.1. Definition and Use of MVS

The purpose of the MVS is to verify and demonstrate that the method and/or analyst is capable of generating precise and accurate analytical data. Method validation samples consist of four replicate aliquots of spiked deionized water prepared and analyzed in a manner identical to samples. The spike concentration should be at the mid-range of the analysis. The samples should be prepared and analyzed in the same batch. They are used to validate new analyst and new instrument performance, and to validate changes in analytical equipment or techniques. MVS requirements are built into NET's internal analyst certification protocols.

### 7.2.2. Frequency of MVS

Method validation must be repeated whenever a significant change in the method or instrumentation is made which could cause the previous MVS to become invalidated. Also, they will be routinely analyzed as part of training and certification of analysts newly performing the analysis.

### 7.2.3. Criteria for MVS

The average percent recovery should pass the interim acceptance criteria applied to the MS/MSD, which is 80-120%, and the relative standard deviation should be within ±20%.

### 7.2.4. Corrective Action for MVS

If a problem is indicated, it must be identified and corrected, and if necessary, MVSs must be re-prepared and re-analyzed. If the problem involves only the instrument, the MVSs must be re-analyzed.

### 7.2.5. Documentation

Since the MVSs serve several purposes, results of the method

validation should be filed either with individual analyst training records, method validation records, or with instrument validation records. How they are filed is dependent on the reason for the study being performed. An alternative would be to file the results jointly and cross reference other files as appropriate. In either case, the data must be retrievable.

## 7.3. Analyst Certification

Each analyst performing this method must successfully complete the requirements detailed in the certification SOP.

## 7.4. Calibration Curve

### 7.4.1. Definition and Use of Calibration Curve

The purpose of a calibration curve is to relate instrument response to sample concentration. It also provides a way of verifying that the instrument response, over a predetermined concentration range, can be predicted using a mathematical equation. If the responses were erratic, there would be no accurate way to relate response to concentration. A three point curve must be run prior to conducting the analysis. The concentrations of the standards should be distributed over the working range of the curve and they should represent the low, mid, and high points of the curve.

### 7.4.2. Frequency of Preparing Calibration Curve

When a daily curve system is used, the curve should be re-prepared if during the analytical run a CCV fails and corrective action is unsuccessful.

### 7.4.3. Criteria for Calibration Curve

A correlation coefficient of 0.995 or greater must be achieved using all calibration standards.

### 7.4.4. Corrective Action for Calibration Curve

Since the calibration curve is used for calculating results for all samples and quality control indicators, an analyte cannot be reported from a run in which the calibration curve did not meet the criteria in Section 7.4.3. Perform any corrective actions necessary, and re-analyze the curve, the samples, and the quality control indicators.

Care should be taken when choosing the concentrations of the standards for the calibration curve. If the intercept is large or if the correlation coefficient is poor, then the concentrations of the standards used in relation to the detection limit and linear range should be carefully evaluated.

7.4.5. Documentation

Raw data associated with constructing a calibration curve should be retrievable and recorded as part of the analytical run.

## 7.5. Initial Calibration Verification Standard (ICVS)

7.5.1. Definition and Use of ICVS

The purpose of the ICVS is to verify that the standards used to make the curve were chemically pure, prepared properly, and that they have not degraded significantly since the time they were made. The ICVS must be from a different source than the calibration standard. The concentrations of the ICVS should be one at the lower end of the curve and one at the higher end of the curve. These standards do not go through sample preparation stages.

The ICVS is sometimes referred to as External Standard or Standard Reference Material (SRM).

7.5.2. Frequency of ICVS

Analyze the ICVS immediately following the calibration curve to verify the curve.

7.5.3. Criteria for ICVS

Acceptance ranges must be +/- 10% of the true value.

7.5.4. Corrective Action for ICVS

If the criteria for the ICVS cannot be met, re-evaluate the calibration curve to verify that all criteria have been met. Verify the acceptability of the source used for preparing the ICVS. Evaluate the concentration of the ICVS compared to the linear range of the analysis and the reporting limit. Recalibrate the instrument and re-analyze the ICV. If none of the above solves the problem, contact your supervisor before proceeding with the analysis.

7.5.5. Documentation

Record the percent recovery of the ICVS on the raw data printout or in the lab book.

## 7.6. Reagent Blank (RB) / Continuing Calibration Blank (CCB)

7.6.1. Definition and Use of Reagent Blank

The reagent blank is a deionized water blank that is subjected to the same conditions that a non-prepared sample undergoes. The reagent blank will determine if any contamination or any memory

effects are occurring. Normally, a reagent blank is analyzed every time a CCVS is analyzed.

7.6.2. Frequency of Reagent Blank

Analyze a minimum of one reagent blank at the beginning and one at the end of each analytical batch. Also, analyze a reagent blank after a minimum of every tenth sample.

7.6.3. Criteria for Reagent Blank

The blank value must be less than the reporting limit.

7.6.4. Corrective Action for Reagent Blank

Since the instrument/calculation is zeroed to the reagent blank, a reagent blank after the tenth sample or at the end of the run having a concentration greater than the reporting limit would indicate a contamination problem or possibly instrument drift. Determine the cause of the high reagent blank value, correct the problem, and re-analyze the samples following the last in control reagent blank/CCVS pair.

An in control reagent blank and an out of control preparation blank would be an indication of a contamination source within the sample preparation procedure.

7.6.5. Documentation

Record the concentration of the reagent blank on the raw data or in the lab book. If the run did not require a preparation blank, enter the end of run reagent blank result into LABSYS2 into the blank entry.

## 7.7. Continuing Calibration Verification Standard (CCVS)

7.7.1. Definition and Use of CCVS

The continuing calibration verification standard is a mid standard that is subjected to the same conditions that a non-prepared sample undergoes. The CCVS will verify that the analytical system is in control with respect to the most recently run calibration curve. Normally, a CCVS is analyzed every time a reagent blank is analyzed.

7.7.2. Frequency of CCVS

Analyze a minimum of one CCVS at the beginning and one at the end of each analytical batch. Also, analyze a CCVS after every tenth sample.

7.7.3. Criteria for CCVS

7.7.3.1. Acceptance criteria requires the percent recovery to be

within 90-110% of the true value.

7.7.3.2. If the analysis does not normally require an LCS to be analyzed, statistical control limits should be generated for the CCVS instead. After a data base of 20-30 points has been collected, calculate the mean expressed as percent recovery and the standard deviation (s).

Upper Control Limit (UCL) = mean + 3s Upper Warning Limit (UWL) = mean + 2s Lower Warning Limit (LWL) = mean - 2s Lower Control Limit (LCL) = mean - 3s

7.7.3.3. The control limits and warning limits are updated yearly or whenever the process is changed. The data from the initial daily CCVS must be plotted on a control chart. The purpose of control charting is to obtain real-time trend analysis of method performance.

Note: A statistical control chart must be generated for either the CCVS or the LCS, but not for both, with a chart for LCS having preference over a chart for CCVS.

7.7.4. Corrective Action for CCVS

If the CCV it is out of control, determine the cause, correct the problem, and re-analyze the samples following the last in control reagent blank/CCVS pair.

7.7.5. Documentation

Record the percent recovery of the CCVS on the raw data or in the lab book.

## 7.8. Preparation Blank (PB)

7.8.1. Definition and Use of PB

The preparation blank is a deionized water blank that is subjected to the same conditions that a prepared sample undergoes. Preparation may include leaching, and/or digestion. The preparation blank is used to demonstrate method performance. A "clean" preparation blank demonstrates that the preparation procedure is free of contamination.

7.8.2. Frequency of PB

Analyze a minimum of one procedure blank per preparation batch. A batch shall contain twenty samples or less.

7.8.3. Criteria for PB

Acceptance criteria requires the procedure blank to be less than the reporting limit.

Procedure blanks are not routinely subtracted from the analytical results.

7.8.4. Corrective Action for PB

7.8.4.1. If a preparation blank shows a detection above the reporting limit for a parameter, then the concentration of the blank vs. the samples in the batch will need to be compared.

7.8.4.2. If the concentration of the blank is above the reporting limit and a sample is greater than 10x the level of the blank, the sample can be reported with a flag indicating method blank contamination.

7.8.4.3. If the concentration of the blank is above the reporting limit and a sample concentration is less than 10x the level in the blank, the sample will need to be re-prepared.

7.8.4.4. If positive values below the reporting limit are observed, they should be evaluated in relation to the sample(s) and extra care should be taken to avoid reporting false positives.

7.8.5. Documentation

Record the concentration of the preparation blank on the raw data or in the lab book.

Enter the preparation blank result into LABSYS2 in the blank entry. If the run did not require a preparation blank, enter the reagent blank result into LABSYS2 instead.

## 7.9. Lab Control Standard (LCS)

7.9.1. Definition and Use of the LCS

The lab control standard is normally a high or mid-level standard that is subjected to the same conditions that a prepared sample undergoes. Preparation may include leaching, and/or digestion. The LCS analysis is designed to serve as a monitor of the efficiency of the entire procedure including sample preparation.

7.9.2. Frequency of LCS

Analyze a minimum of one LCS per batch. A batch shall contain twenty samples or less.

7.9.3. Criteria for LCS

7.9.3.1. Interim acceptance criteria requires the LCS to be within 80-120% of the true value.

7.9.3.2. After a data base of 20-30 points has been collected,

calculate the mean expressed as percent recovery and the standard deviation (s).

Upper Control Limit (UCL) = mean + 3s Upper Warning Limit (UWL) = mean + 2s Lower Warning Limit (LWL) = mean - 2s Lower Control Limit (LCL) = mean - 3s

7.9.3.3. The control limits and warning limits are updated yearly or whenever the process is changed. The data must be plotted on a control chart. If the analysis does not normally require an LCS, then CCVS should be charted instead. The purpose of control charting is to obtain real-time trend analysis of method performance.

7.9.4. Corrective Action for LCS

The inability of the laboratory to successfully analyze the LCS indicates a problem potentially related to the sample preparation procedures. This is especially true if the CCVSs were all in control. If the control windows are exceeded, all sample results associated with the LCS are suspect and should be re-prepared and reanalyzed, after the cause of the problem has been determined and corrected. If reanalysis of the sample occurs outside holding times or if insufficient sample is available for reanalysis, the results must be flagged and the LCS reported to the client.

7.9.5. Documentation

Record the percent recovery on the raw data or in the lab book. Enter the percent recovery of the LCS into LABSYS2 in the LCS entry.

## 7.10. Matrix Spike / Matrix Spike Duplicate (MS/MSD)

7.10.1. Definition and Use of MS/MSD

The matrix spike / matrix spike duplicate pair are two separate aliquots of sample which are spiked with known concentrations of analyte and subjected to the same conditions that a sample undergoes. The recommended spike concentration should be 20% of the top standard or equal the low or mid standard from a three point curve performed the day of the analysis. These data are generated to determine long-term precision and accuracy of the analytical method on various matrices. These data alone cannot be used to evaluate the precision and accuracy of individual samples except for the sample chosen for the MS/MSD analysis.

7.10.2. Frequency of MS/MSD

Analyze a minimum of one MS/MSD pair per every analytical batch per matrix; the two matrices monitored are water and soil. An analytical batch is twenty samples or less.

7.10.3. Criteria for MS/MSD

7.10.3.1. The calculation for accuracy is:

$$\text{Accuracy} = \frac{(\text{Spiked Sample}) - (\text{Original Sample})}{\text{Spike Value}} \times (100)$$

7.10.3.2. The calculation for Precision as Relative Percent Difference (RPD) is:

$$\text{RPD} = \frac{(\text{Larger Value} - \text{Smaller Value}) \times 100}{\text{Sum of the Values} / 2}$$

Precision (RPD) must be less than 20%.

7.10.3.3. Advisory interim acceptance criteria requires the MS/MSD percent recovery to be within 75-125% and the relative percent difference to be less than 20.

7.10.3.4. After a data base of 20-30 points of a given matrix, i.e. aqueous and soils, have been collected, calculate the mean expressed as percent recovery and the standard deviation (s).

Upper Control Limit (UCL) = mean + 3s Upper Warning Limit (UWL) = mean + 2s Lower Warning Limit (LWL) = mean - 2s Lower Control Limit (LCL) = mean - 3s

7.10.3.5. The control limits and warning limits are updated yearly or whenever the process is changed. The data must either be tabulated or plotted on a control chart. At a minimum, statistical control and warning limits must be calculated separately for aqueous and soil matrices. These are advisory limits.

7.10.4. Corrective Action for MS/MSD

No action is taken on out of control MS/MSD data alone to qualify an entire batch. Action taken must be weighed carefully since it may be difficult to determine if poor precision and/or accuracy is a result of sample non-homogeneity/uniqueness, method defects, or laboratory technique. However, the data may be used in conjunction with other QC criteria to determine the need for qualifying the data. The following applies when the LCS is in control:

If the MS is in control and the MSD is out of control (or vice-versa), and the RPD is **not** acceptable, then the data is suspect. The analysis is suspect and an investigation should be made to determine an assignable cause for the unacceptable RPD. Documentation of an

assignable cause is essential.

If the MS and MSD is out of control and the RPD is not acceptable, the scope of the implication must be evaluated. If the sample is part of a project, i.e., many samples from the same site/same client, the client should be contacted.

MS/MSD data out of control indicates potential matrix problems. The following procedure can be used to determine the scope of the interference for metals analyses which appear to have matrix problems:

Note: Use of the following procedure is not mandatory. It is up to each division to decide whether to incorporate the following procedure into their routine.

1) Perform a post digestion spike on the sample. If the post digestion spike falls within 85-115% of the true value, then the indication is that the matrix interference is limited in scope. If the post digestion spike does not fall within 85-115% two options exist.

a) If the original sample result was less than the detection limits, and the post-digestion spike was less than 85%, it is possible that the result is skewed due to negative interference. If the original sample result was positive, and the post-digestion spike was greater than 115%, it is possible that the result is skewed due to positive interference. Verify/estimate scope of a negative or positive interference by analyzing a post digestion spike on a diluted sample aliquot. The original MS/MSD results must be reported in LABSYS and flagged, indicating that the recoveries were not within the acceptable range. If the above scenario was followed issue appropriate notification to the client in a cover letter or case narrative submitted with the final report.

b) Alternatively, re-analyze the sample using the method of standard additions (MSA) as detailed in Section 7.12. Note: GFAA analyses do not require duplicate injections when MSA is the analytical technique used for quantification.

## 7.11. Reporting Limit Verification Standard

### 7.11.1. Definition and Use of RLVS

The RLVS provides information regarding instrument performance at or near the reporting limit. The concentration of the RLVS should equal the reporting limit. If the reporting limit is close to the method detection limit, it may be necessary to raise the RLVS by a factor of 2-5.

### 7.11.2. Frequency of RLVS

Analyze this standard after performing instrument calibration. In some cases, it may be possible to incorporate the RLVS standard into the calibration curve. The reporting limit is often part of the curve so that more reliability can be obtained for the reporting limit. Should the curve include a point which is at or below the reporting limit, the reporting limit verification standard will not be performed.

7.11.3. Criteria for RLVS

Advisory, acceptance criteria requires the percent recovery to be within ± 30% of the true value.

7.11.4. Documentation

Record the percent recovery on the raw data or in the lab book.

**7.12. Method of Standard Addition (MSA)**

The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards.

7.12.1. To begin analysis by MSA, the sample must first be diluted two fold. This is read as a zero concentration. Next, three additional spikes of the sample are prepared at increasing intervals using 1 part of the sample added to 1 part of the spiking solution. A curve is then produced by plotting the concentrations of the spikes versus the absorbance obtained. The curve should have a slope that is within 20 % of the standard curve. The negative value of the y-intercept is then obtained. The negative y-intercept is then multiplied by the dilution factor to obtain the final result.

# 8. REFERENCES

8.1. Methods for Chemical Analysis of Water and Wastes, USEPA, Environmental Monitoring and Support Laboratory EPA-600/4-79-020

8.2. Standard Methods For the Examination of Water and Wastewater, 18th Edition, APHA

8.3. Test Methods for Evaluating Solid Waste, 3rd Edition, July 1992.

8.4. Pre-existing internal documents (SOPs) from the various NET divisions were used as resources/references during the preparation of this document. These documents are on file at the Corporate office.

Footnote 1 and 2: Richard D. Beaty, Concepts, Instrumentation and Techniques in Atomic Absorption - Perkin Elmer.

Footnote 3: Analytical Methods for Graphite Tube Atomizers - Varian.

8.5. SIMAA 6000 Software Guide - Perkin Elmer 1994

8.6. SIMAA 6000 Installation, Maintenance, System Description Release 1.1 February, 1995.

## APPENDIX 1.

PREPARATION OF STANDARD:

| VOLUME | OF SOLUTION | DILUTE TO | = CONC | |
|---|---|---|---|---|
| Step 1: | Working Standard | | | |
| 10 mL | PE Multi-Element Atomic Spectroscopy Standard | 1000 mL | 1000 | ug/L Pb |
| | | | 1000 | ug/L Tl |
| | | | 1000 | ug/L Se |
| | | | 1000 | ug/L Sb |
| | | | 1000 | ug/L As |
| | | | 1000 | ug/L Al |
| | | | 500 | ug/L Ba |
| | | | 500 | ug/L Co |
| | | | 500 | ug/L Cu |
| | | | 500 | ug/L Ni |
| | | | 200 | ug/L Cr |
| | | | 200 | ug/L Mn |
| | | | 200 | ug/L Fe |
| | | | 100 | ug/L Ag |
| | | | 50 | ug/L Cd |
| | | | 50 | ug/L Be |
| Step 2: | Calibration Standard | | | |
| 10 mL | Working Standard | 100 mL | 100 | ug/L Pb |
| | | | 100 | ug/L Tl |
| | | | 100 | ug/L Se |
| | | | 100 | ug/L Sb |
| | | | 100 | ug/L As |
| | | | 100 | ug/L Al |
| | | | 50 | ug/L Ba |
| | | | 50 | ug/L Co |
| | | | 50 | ug/L Cu |
| | | | 50 | ug/L Ni |
| | | | 20 | ug/L Cr |
| | | | 20 | ug/L Mn |
| | | | 20 | ug/L Fe |
| | | | 10 | ug/L Ag |
| | | | 5 | ug/L Cd |
| | | | 5 | ug/L Be |

Step 3: Low Calibration Standard

| | | | | |
|---|---|---|---|---|
| 10 mL | Calibration Standard | 100 mL | 10 | ug/L Pb |
| | | | 10 | ug/L Tl |
| | | | 10 | ug/L Se |
| | | | 10 | ug/L Sb |
| | | | 10 | ug/L As |
| | | | 10 | ug/L Al |
| | | | 5 | ug/L Ba |
| | | | 5 | ug/L Co |
| | | | 5 | ug/L Cu |
| | | | 5 | ug/L Ni |
| | | | 2 | ug/L Cr |
| | | | 2 | ug/L Mn |
| | | | 2 | ug/L Fe |
| | | | 1 | ug/L Ag |
| | | | 0.5 | ug/L Cd |
| | | | 0.5 | ug/L Be |

FURNACE - MULTI-ELEMENT ICV

NOTE: ALL ICV'S ARE PREPARED IN 6% NITRIC ACID. (USE ALTERNATE SOURCE)

| VOLUME | OF SOLUTION | DILUTE TO | = CONC | |
|---|---|---|---|---|
| Step 1: Working ICV Standard | | | | |
| 10 mL | PE Multi Element Atomic Spectroscopy Standard | 1000 mL | 1000 | ug/L Pb |
| | | | 1000 | ug/L Tl |
| | | | 1000 | ug/L Se |
| | | | 1000 | ug/L Sb |
| | | | 1000 | ug/L As |
| | | | 1000 | ug/L Al |
| | | | 500 | ug/L Ba |
| | | | 500 | ug/L Co |
| | | | 500 | ug/L Cu |
| | | | 500 | ug/L Ni |
| | | | 200 | ug/L Cr |
| | | | 200 | ug/L Mn |
| | | | 200 | ug/L Fe |
| | | | 100 | ug/L Ag |
| | | | 50 | ug/L Cd |
| | | | 50 | ug/L Be |

Step 2: Calibration ICV Standard

| | | | | |
|---|---|---|---|---|
| 6 mL | Working ICV Solution | 100 mL | 60 | ug/L Pb |
| | | | 60 | ug/L Tl |
| | | | 60 | ug/L Se |
| | | | 60 | ug/L Sb |
| | | | 60 | ug/L As |
| | | | 60 | ug/L Al |
| | | | 30 | ug/L Ba |
| | | | 30 | ug/L Co |
| | | | 30 | ug/L Cu |
| | | | 30 | ug/L Ni |
| | | | 20 | ug/L Cr |
| | | | 20 | ug/L Mn |
| | | | 20 | ug/L Fe |
| | | | 6 | ug/L Ag |
| | | | 3 | ug/L Cd |
| | | | 3 | ug/L Be |

**Preparation of Spiking Solutions and Digested Standards**

FURNACE MULTI-ELEMENT SPIKING & DIGESTED STANDARD

NOTE: All Standards are prepared in 6% Nitric Acid.

Use 1 mL of the GFAA 1.0 mg/L Working Stock Standard solution for each 50 mL of sample. For Cd and Be dilute the 1.0 mg/L solution 1:10. Use 1 mL of this for each 50 mL aliquot of sample.

| ELEMENT | CONCENTRATION SPIKING SOL. (mg/L) | CONCENTRATION FINAL (mg/L) |
|---|---|---|
| Cr | 0.20 | 0.008 |
| Co | 0.50 | 0.020 |
| Pb | 1.00 | 0.040 |
| Tl | 1.00 | 0.040 |
| Cd | 0.05 | 0.002 |
| Be | 0.05 | 0.002 |
| As | 1.00 | 0.040 |
| Se | 1.00 | 0.040 |
| Ag | 0.10 | 0.004 |

Shelf Life of Calibration and Spiking Standards

1000 ppm Standards - whichever is the earlier date 6 Months from date of opening 1 year from receipt unopened expiration date on bottle from manufacturer

Stock Solutions: Furnace 1 Month

Working Standards: Furnace 1 Week

Spiking Solutions:

Three months from date of preparation if not purchased; if spiking solution purchased, 1 year from date of opening or expiration date on bottle (earliest date).

# DRINKING WATER APPENDIX - GFAA

For the analysis of potable samples, all calibration, sample handling and quality control procedures in this SOP must be followed with the addition of the following potable-specific procedures.

## 1. Sample Turbidity Screen

Sample turbidity must be determined for every potable sample in accordance with the procedures in the Turbidity Screen SOP.

### 1.1. Criteria

Samples with turbidity $\geq$ 1.0 NTU must be digested in accordance with the appropriate digestion SOPs prior to analysis. Samples with turbidity < 1.0 NTU may be analyzed without digestion. If the sample reads < 1.0 NTU, but particulate matter is visible in the sample, then the sample must be digested prior to analysis.

## 2. Sample pH

The pH of each potable sample must be determined to be < 2 prior to analysis. If the sample is preserved at the laboratory, then the sample must be held a minimum of 16 hours after preservation before the pH is taken and analysis is performed.

## 3. Reporting Limit Check (RLC) samples

A low level standard (RLC) with a concentration less than or equal to the Ohio EPA reporting limit is analyzed to validate the calibration at or near the reporting limit. If one of the calibration standards is at or below the OEPA minimum reporting level, then an RLC is not required.

### 3.1. Frequency And Criteria

The RLC is analyzed after each calibration. Acceptance criteria is +/- 30% of the true value.

### 3.2. Corrective Action

If the criteria cannot be met, re-evaluate the calibration curve and verify the acceptability of the source used for preparing the RLC. If necessary, repeat the calibration and reanalyze the RLC. All elements being analyzed must have an acceptable RLC for potable analysis.

## 4. Independent Calibration Verification Standards (ICVS)

Both a high and a low concentration ICVS from a source separate from that used for instrument calibration must be analyzed to verify instrument calibration. Concentrations of the low ICVS are listed in Appendix 1. The high ICVS is 5 times the low ICVS concentration.

**4.1. Frequency And Criteria**

The high and low ICVS must be analyzed at the beginning of the run, following calibration, and at the end of the run. Acceptance criteria is +/- 10% of the true value.

**4.2. Corrective Action**

If the acceptance criteria cannot be met, re-evaluate the calibration curve and verify the acceptability of the source used for preparing the ICVS. If necessary, repeat the calibration curve and reanalyze the ICVS. All elements being analyzed must have an acceptable ICVS for potable analysis. If the final ICVS does not meet acceptance criteria, then no data bracketed by the last acceptable Calibration Check Verification Standard (CCVS) can be reported.

**5. Duplicates**

Samples must be analyzed in duplicate to verify replication of analysis.

**5.1. Frequency And Criteria**

Duplicates must be analyzed at a frequency of 10% of samples analyzed. Acceptance criteria is reproducibility of results within +/- 20% for analyte concentrations greater than the OEPA minimum reporting limits.

**5.2. Corrective Action**

Poor reproducibility of sample results is indicative of matrix interferences or a lack of sample homogeneity. The sample should be diluted and analysis repeated.

**6. Matrix Spikes (MS)**

Matrix spikes are representative sample aliquots which are spiked with known concentrations of analyte. The concentrations of the matrix spike are listed in Appendix 1.

**6.1. Frequency And Criteria**

Each sample for potable analysis must be matrix spiked. Acceptance criteria is +/- 15% of the true value for samples with analyte hits and +/- 20% of true value for samples with no analytes detected.

**6.2. Corrective Action**

If the concentration of the analyte is more than 4 times that of the spike, then the spiking level is considered insignificant, and skewed recoveries may result. If the matrix spike sample must be diluted to be brought into calibration range, then the spike may be diluted out resulting in low recoveries. While no action is required based on matrix spike recovery alone, the data must be reviewed carefully in conjunction with the other quality control indicators (QCIs).

## 7. Graphite Program Replicates

For GFAA analysis of potable samples, each sample may be analyzed with a single replicate, or burn, since each sample is matrix spiked.